Removal of Natural Organic Matter from Different Raw Waters by Ion Exchange Resins

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Abstract
Most South African water treatment plants utilise surface water sources whose quality is continuously compromised due to high return flows and indirect reuse. The water treatment methods used by these plants are based on the removal of turbidity, various chemical contaminants and microorganisms. Recently introduced NOM regulations added the removal of natural organic matter (NOM) as a priority. Basic anion exchange resins can be used to remove NOM. This paper reports this method of NOM removal. Due to the variability in the composition of NOM in natural raw water, eight surface waters were collected throughout South Africa as representative of the different water types of the country. Two resins were used for this study, a strong and a weak – base anion resins. They were chosen for their availability and competitive price at the local market. NOM removal in raw water was quantified by measuring ultraviolet absorbance at a wavelength of 254 nm (UV 254), dissolved organic carbon (DOC) and by calculating the specific ultraviolet absorbance (SUVA) at 254 nm. The Freundlich equilibrium isotherms were also fitted and the Freundlich parameters determined. (Add summary of results)

INTRODUCTION

Most South African water treatment plants utilise surface water sources whose quality is continuously compromised due to high return flows and indirect reuse. The water treatment methods used by these plants are based on the removal of turbidity, various chemical contaminants and microorganisms. Recently introduced NOM regulations added the removal of natural organic matter (NOM) as a priority.

Natural organic matter (NOM) is a complex and heterogeneous mixture of organic materials such as humic acids, fulvic acids, low molecular weight acids, proteins, aminoacids and carbohydrates (Cornelissen et al., 2008). In natural water NOM results from the degradation of plants, animals and microorganisms. If not properly removed in water NOM compounds create many problems such as (Ødegaard et al., 2010):

- Organoleptic aspects of water (odour, colour and taste);
- Reduction of disinfectants power in water by reacting with them;
- Production of disinfection by-products (DBPs) which some are health hazards (Melnick et al., 2007);
- Negative impact on the removal of inorganic ions;
- Impact on the quantity of coagulant used for treatment purposes;
- Control of coagulation conditions and performance;
- Impact on the corrosion processes of the drinking water pipelines;
- Contribute to bacterial regrowth in the distribution network (Van der Kooij, 1999);
- Create membrane fouling;
- React with some chemicals to form complexes and therefore increase the mobility of those chemicals;
- Decrease the adsorption capacity of the activated carbon by fouling the pores;

- Lead to poor oxidation of manganese and iron (Cornelissen et al., 2008).

Various methods are used to remove NOM in water including (Melnick et al., 2007):
- Nano-filtration: consists of removing large molecules of NOM from water by molecular sieving;
- Oxidation: the molecules of NOM responsible for colour are characterized by double carbon bonds C=C. A strong oxidant is used to break those bonds;
- Biofiltration: consists of using strong oxidants to break large molecules into biodegradable components that can be removed by biofiltration;
- Adsorption: use of activated carbon to remove small neutral hydrophobic NOM molecules;
- Coagulation: used to remove large anionic molecules of NOM. It is the most widely used NOM removal method worldwide;
- Ion exchange: consists of using anionic resins to remove small anionic molecules as well as hydrophilic charged molecules.

In this study we use the ion exchange method to investigate the removal of NOM from different waters by two resins.

Ion exchange mechanism:
Tan and Kilduff (2007) explained that two mechanisms are involved in the removal of NOM when using ion exchange resins including:
- Ion exchange which consists of exchange of ions from the resin (solid phase) and water (liquid phase) and ionic interactions between the ionic functional groups and the ions from the liquid phase;
- Physical adsorption by the van der Waals forces between the non-ionic (hydrophobic) molecules of NOM and the resin polymer matrix.

It has been observed that the sorption process is influenced by the pH. At high pH the dominant mechanism is ion exchange while at neutral pH physical adsorption also plays a role (Croué et al., 1999). However, the most important removal mechanism with resin is ion exchange rather than adsorption (Tan et al., 2005). Boyer and Singer (2008) conducted a series of experiments using NOM-model waters. By adding Suwannee River Fulvic Acid; they found that the only mechanism of NOM removal by resin was ion exchange.

Resins characteristics have an impact on NOM removal. The impacts of some characteristics are explained below:
- Resin pore size: large pore macroporous resins remove more large fractions of NOM while with the small pore size resins, the removal of large fractions of NOM is small. This because larger pores are easily penetrated by large size NOM compounds (Bolto et al., 2002).
- Resin structure: Bolto et al. (2002) found that on overall a resin with macroporous structure removes more than a gel one. This is explained by the fact that NOM compounds like humic acids diffuse better in a macroporous structure (Bolto et al., 2002; Cornelissen et al., 2008). However, Tan et al. (2005) found that a strong base resin of gel structure removes more NOM than the macroporous structure and explained that the gel matrix has the ability to swell in water facilitating its accessibility to large NOM molecules.
- Water content: the higher the water content the higher the uptake of NOM regardless of the resin structure. This is due to the fact that, when water content is high, there are more open structures that allow an easy entry of the large NOM components (Bolto et al., 2002).

Inorganic ions in water also play a role by enhancing or inhibiting the NOM uptake by the resin. Some ions of importance are sulphates, whose presence reduces NOM removal (Boyer and Singer, 2006), as well as sodium ions, which have the same effect. Chloride and calcium ions, however, increase NOM removal when present.

EXPERIMENTAL PROCEDURES

Materials

Anionic exchange resins.
The choice of a resin is based on many criteria including (Thomas and Crittenden, 1998): equilibria data and kinetics properties, the regeneration process (if it is not to be discarded after use), its availability and price, as well as other characteristics such as strength, chemical resistance etc. Two resins were selected based on their availability and competitive price on the local market. They are designed to remove organic substances including NOM and their characteristics are outlined in Table 1 below.

Table 1. Characteristics of ion exchange resins selected

Resin	Type	Structure	Material	Capacity (eq/l)	Water content (%)	Average resin size (mm)	pH Range
LEWATIT MonoPlus MP 600	Strong base	MP*	polystyrene	1.1	55 – 60	0.6 (+/- 0.05)	0 – 14
LEWATIT MP 62	Strong base	MP*	polystyrene	1.7	50 – 55	0.315 – 1.25	0 – 8

* MP: Macroporous

Water samples.
With the aim of treating different water types, eight natural waters were collected at different water treatment plants throughout South Africa as a representative of the different types of the waters of the country, as listed in Table 2 below.

Table 2. Raw waters

Raw water name	Date of collection		
	Aout	September	November
	Round 2	Round 3	Round 4
Loerie(Water Treatment Plant)	L		
Olifantsvlei(Wastewater Treatment Plant)	O		
Plettenberg Bay Water Treatment Plant	P		
Rietvlei Water Treatment Plant	R		
Stilfontein(Water Treatment Plant)	S		
Umzoniana(Water Treatment Plant)	U		
Vereeniging (Water Treatment Plant)	V		
Wiggins (Water Treatment Plant)	W		

Methods

Resin pretreatments.
The pretreatment of the weak resin (MP 62) was as follows:
Nneutralization with an excess of 2% NaOH solution for 24 hours followed by conditioning with an excess of 3.7% HCl solution for 24 hours. After neutralization the resin was rinsed by demineralized water for 2 hours. Once conditioned, the resin was rinsed several times with an excess of water for 24 hours. A pump was used to dry the resin and at last air-dried overnight before use.
The pretreatment of the strong resin (MP 600) consisted of air-drying the resin beads overnight prior to use.

Batch experiments.
For both resins the following procedure was used:
- Measure 10, 25, 60, 135 and 320 mg of resin (air-dried mass)
- Pour into a 500 ml Erlenmeyer containing 250 ml of raw water to be treated. The resin concentration, therefore, becomes 40, 100, 240, 540 and 1280 mg/l.
- The resin solutions are mixed on a shaker table at 140 u/min for 72 hours (three days) at an average room temperature of 25ºC. Although the time to remove 50% of NOM compounds with resins varies between 7 to 10 minutes (Bolto et al., 2002), a longer time (72 hours) was opted to allow large size NOM molecules to have time to react with the resin beads (Bolto et al., 2002).
- Filter the resulting treated waters through a 0.45 μm filter before measuring UV absorbance at 254 nm with a spectrophotometer (Ultrospec II UV/Visible). DOC concentration of each sample was also was determined by the TOC analyzer (Teledyne Tekmar, TOC fusion), and specific ultraviolet absorbance (SUVA) at 254 nm was also calculated.

Freundlich isotherm equation.
The Freundlich isotherm equation was selected because it is better suited for aqueous solutions (Sontheimer et al., 1988). The Freundlich equation used is presented below:

$qe = K\ Ce^{n}$

qe: NOM concentration in solid (per m per mg/L or $m^{-1}\ mg^{-1}\ L$)
Ce: NOM concentration in water (per m or m^{-1})
K: Freundlich constant ($m^{n-1}\ mg^{-1}\ L$).
n: Freundlich exponent (-)

The two Freundlich parameters (K and n) are related to the capacity and the affinity of the resin for NOM molecules respectively (Cornelissen et al., 2008). For the same n-value, the sample with greater K means there is a greater capacity for NOM and, for the same K-value, the sample with greater n has the highest affinity for NOM components.

RESULTS AND DISCUSSION

Raw waters
Most natural waters were basic with pH ≥ 8. This was detrimental for the weak base resin which performs at pH-values less than 8.

The concentrations of sulfate and sodium ions were high and their action is to decrease NOM removal, while the chloride and calcium ions (whose actions are to enhance NOM removal)

were also in substantial concentration. The concentrations of other elements such as iron (Fe), manganese (Mn), aluminium (Al), potassium (K), ortho-phosphate (P), nitrate, nitrite and ammonia (as N) were very small, thus not affecting the removal process. See Table 3.

Table 3. Raw water characteristics

	R	V	S	O	P	U	W	L
Sulphate as SO_4								
Sodium as Na								
Chloride as Cl								
Calcium as Ca								
Iron as Fe								
Manganese as Mn								
Aluminium as Al								
Potassium as K								
Ortho-phosphate as P								

Batch experiments

The values of the Freundlich parameters determined from the Freundlich equilibrium isotherms are presented in Tables 4 and 5. The K values for the strong resin were greater than those for the weak resin suggesting that the NOM removal capacity of the strong resin is greater than that of the weak resin used. The comparison of the Freundlich exponent values for n did not give any specific information suggesting that both resins have almost the same degree of affinity for NOM molecules.

Table 4. Freundlich parameters for the raw water with the weak base resin MP 62

	Round 2			Round 3			Round 4		
	K	n	R^2	K	n	R^2	K	n	R^2
R	2.41E-04	2.852	0.953	4.88E-04	2.080	0.986	4.74E-04	0.993	0.995
V	2.56E-06	4.217	0.885	3.81E-03	1.059	0.959	5.07E-05	2.96	0.934
S	3.37E-05	3.807	0.989	3.16E-04	2.307	0.971	9.16E-03	0.914	0.909
O	2.01E-05	3.931	0.968	3.33E-04	2.274	0.982	1.79E-05	4.48	0.885
P	7.10E-03	0.82	0.976	8.57E-03	0.720	0.958	1.04E-02	0.54	0.744
U	8.71E-05	3.116	0.998	6.30E-04	2.100	0.96	1.56E-03	1.718	0.901
W	5.09E-07	9.441	0.962	2.21E-05	5.307	0.982	4.90E-04	2.08	0.986
L	4.79E-05	3.721	0.983	6.85E-03	1.770	0.885	3.41E-03	1.657	0.793

Table 5. Freundlich parameters for the raw waters with the strong base resin MP 600

	Round 2			Round 3			Round 4		
	K	n	R^2	K	n	R^2	K	n	R^2
R	3.41E-04	3.073	0.887	8.07E-06	4.87	0.981	2.70E-03	1.88	0.75
V	2.03E-11	11.14	0.851	1.72E-08	13.9	0.973	3.62E-07	8.842	0.935
S	2.03E-04	3.399	0.94	9.13E-03	0.808	0.97	1.79E-02	0.511	0.983
O	1.99E-04	3.336	0.926	5.86E-05	5.046	0.978	3.82E-06	5.192	0.890
P	1.09E-02	0.876	0.914	3.12E-05	4.26	0.997	3.07E-03	1.663	0.889
U	1.19E-04	4.037	0.856	3.46E-06	6.393	0.941	7.76E-07	6.880	0.883
W	6.30E-05	5.796	0.964	2.45E-04	2.557	0.896	1.65E-03	1.779	0.835
L	2.42E-04	2.948	0.942	9.96E-05	5.125	0.916	1.86E-03	2.454	0.768

The percentage of absorbance removal differs when the dosage of both resins is small. At 100 mg/L of resin, the UV absorbance removal for the weak resin is approx. 40% (range 35% - 46%), while the strong resin absorbance removal is approx.58% (range 55% - 61%). However, when the resin concentration is increased to 1280 mg/L, the average percentage of absorbance removal is the same at 76% (range 72% - 79% for the weak resin and, 74% - 77% for the strong resin). This can be explained by the fact that there are more available sites with the increase of resin dosage. See Figure 1.

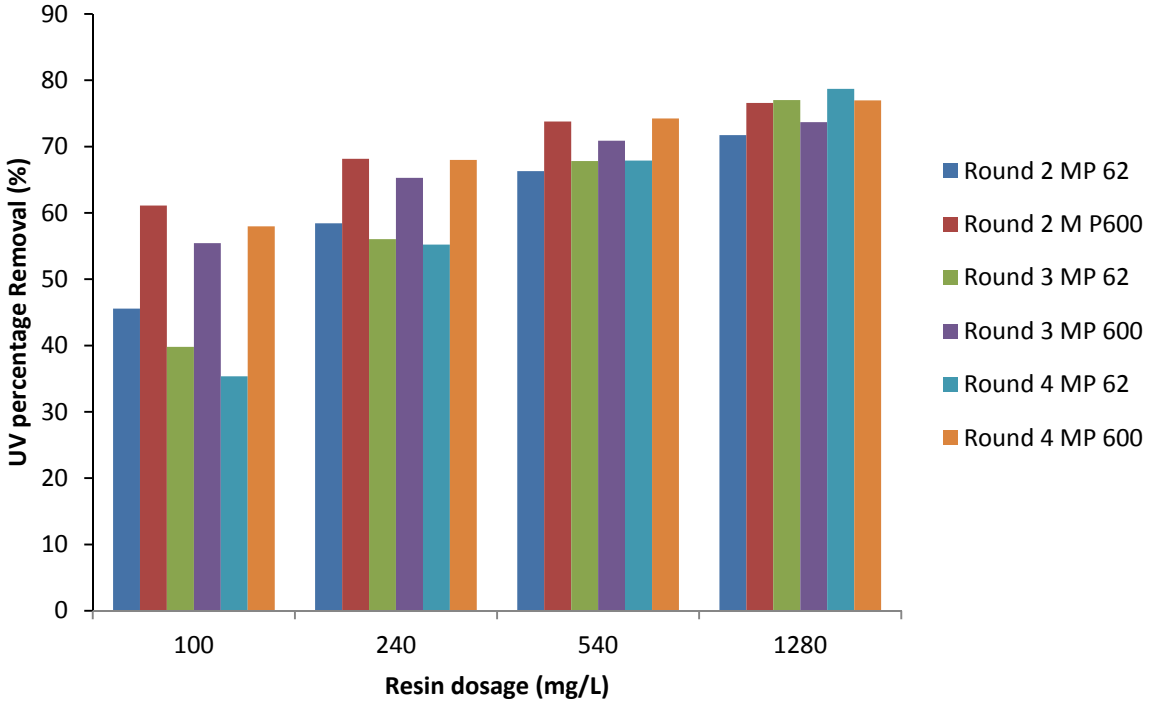

Figure 1. Average percentage UV removal

Although the Freundlich parameters were different from one round to another when treating raw waters with the same resin, it appears that the isotherms positions were very similar. See Figures 2, 3 and 4 for the weak resin.

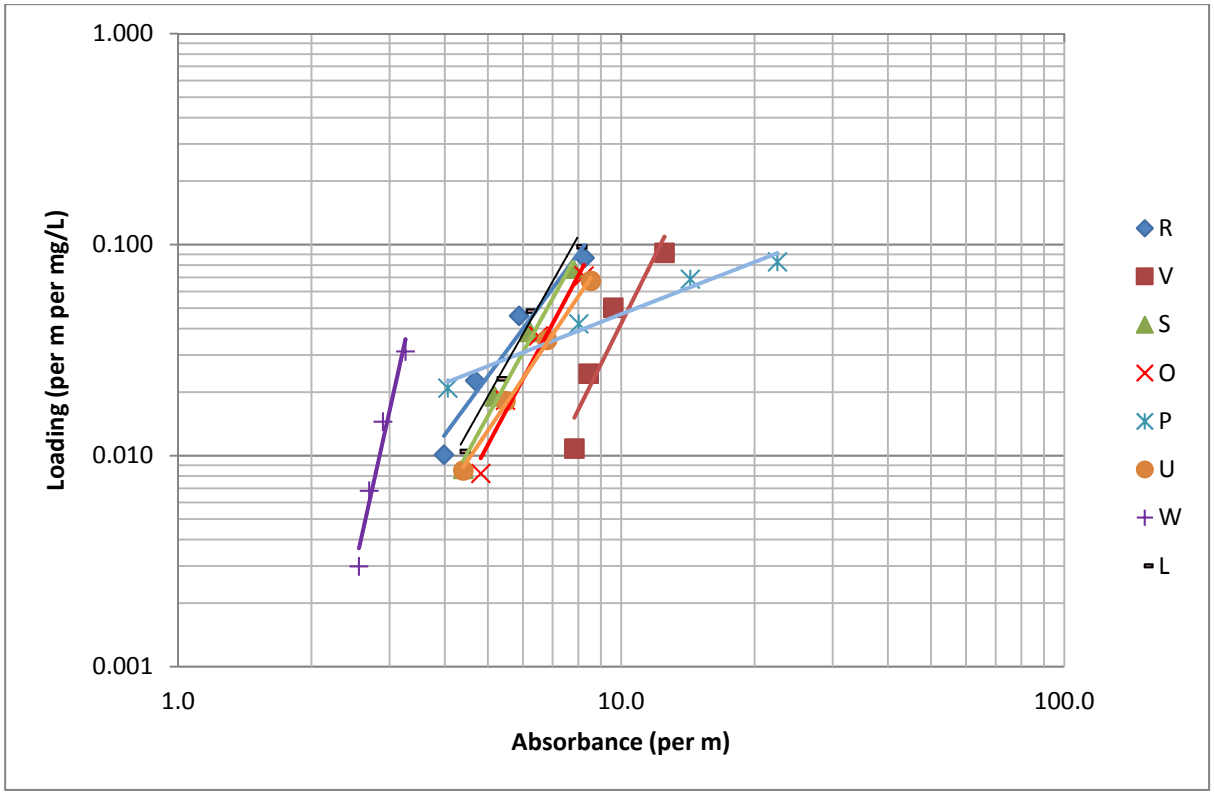

Figure 2.Freundlich isotherms with MP 62 for round 2 samples.

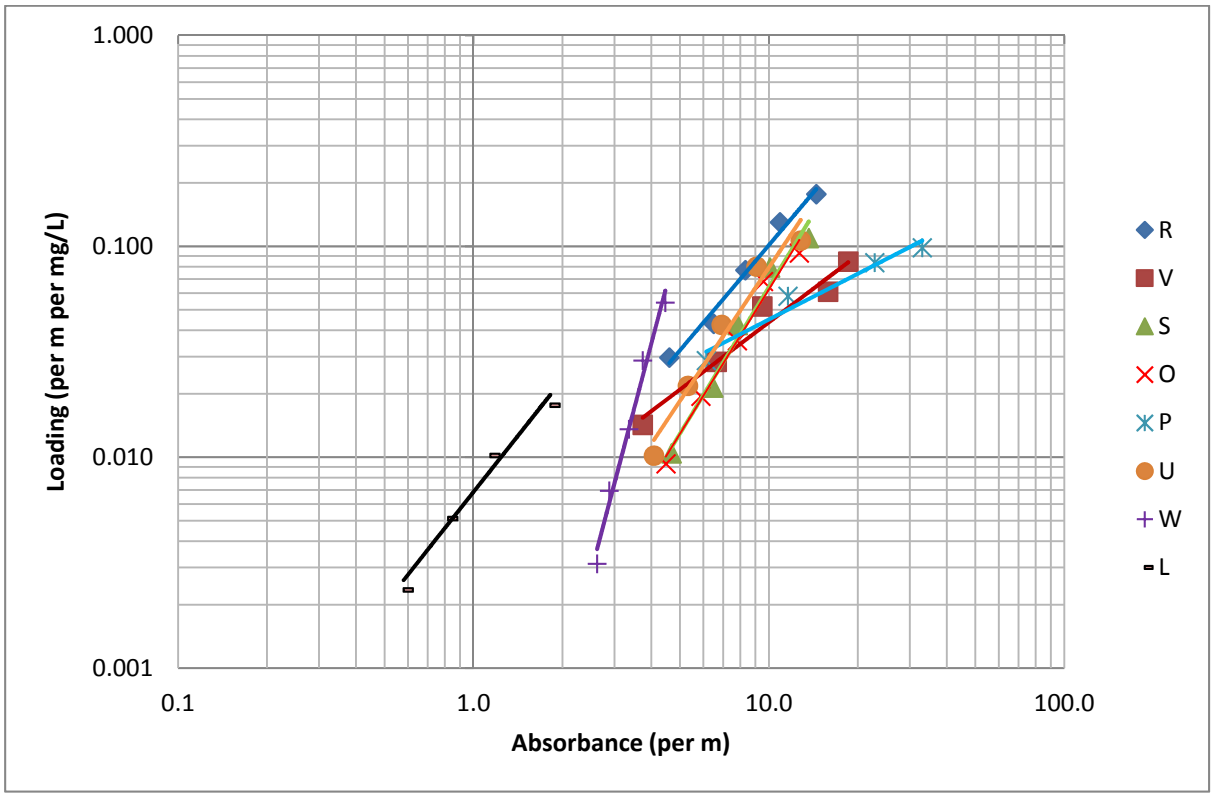

Figure 3.Freundlich isotherms with MP 62 for round 3 samples.

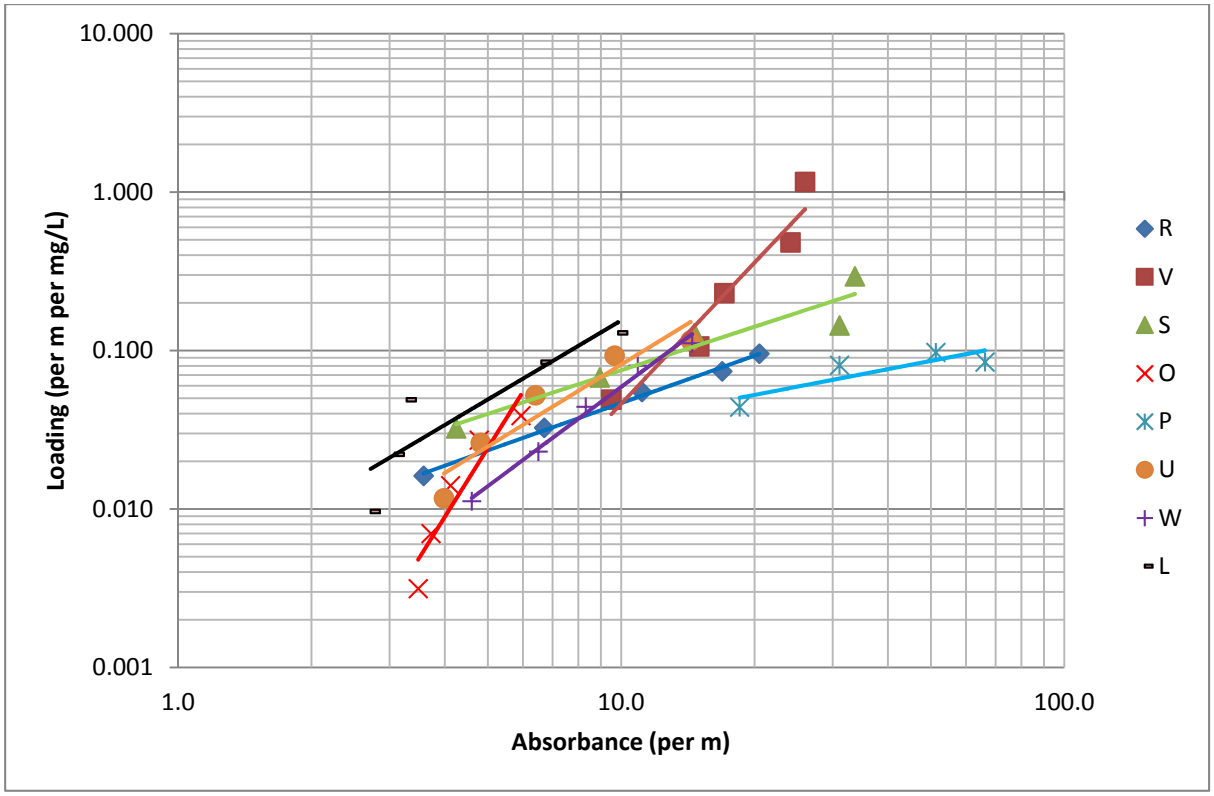

Figure 4: Freundlich isotherms with MP 62 for round 4 samples.

The figures show that all the isotherms are situated at the same places, the same range of values. This indicates that natural raw waters collected at different periods of time react the same way to the same resin. The values of K and n are different, which can be attributed to the seasonal variation of NOM as found by Sharp et al. (2006) and Uyak et al. (2008).

The same trend was observed when natural waters were treated with the strong resin MP 600. See Figures 5, 6 and 7.

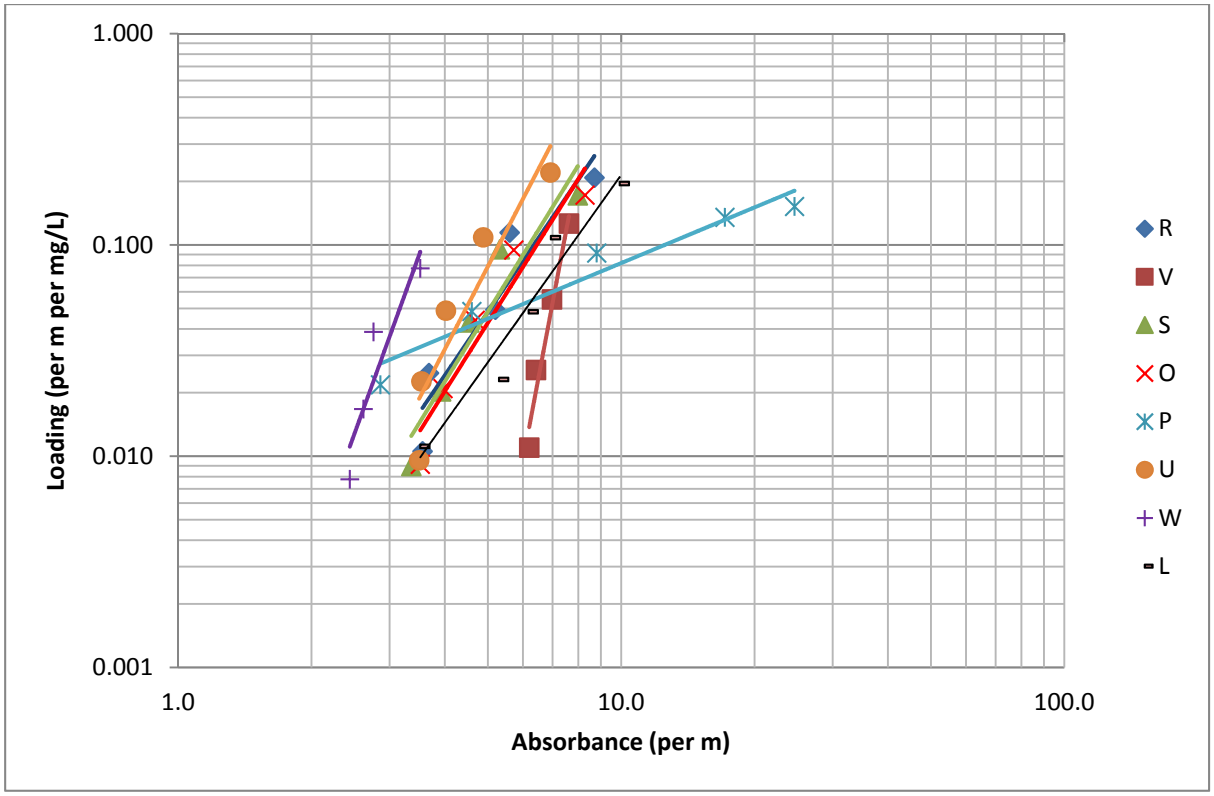

Figure 5. Freundlich isotherms with MP 600 for round 2 samples.

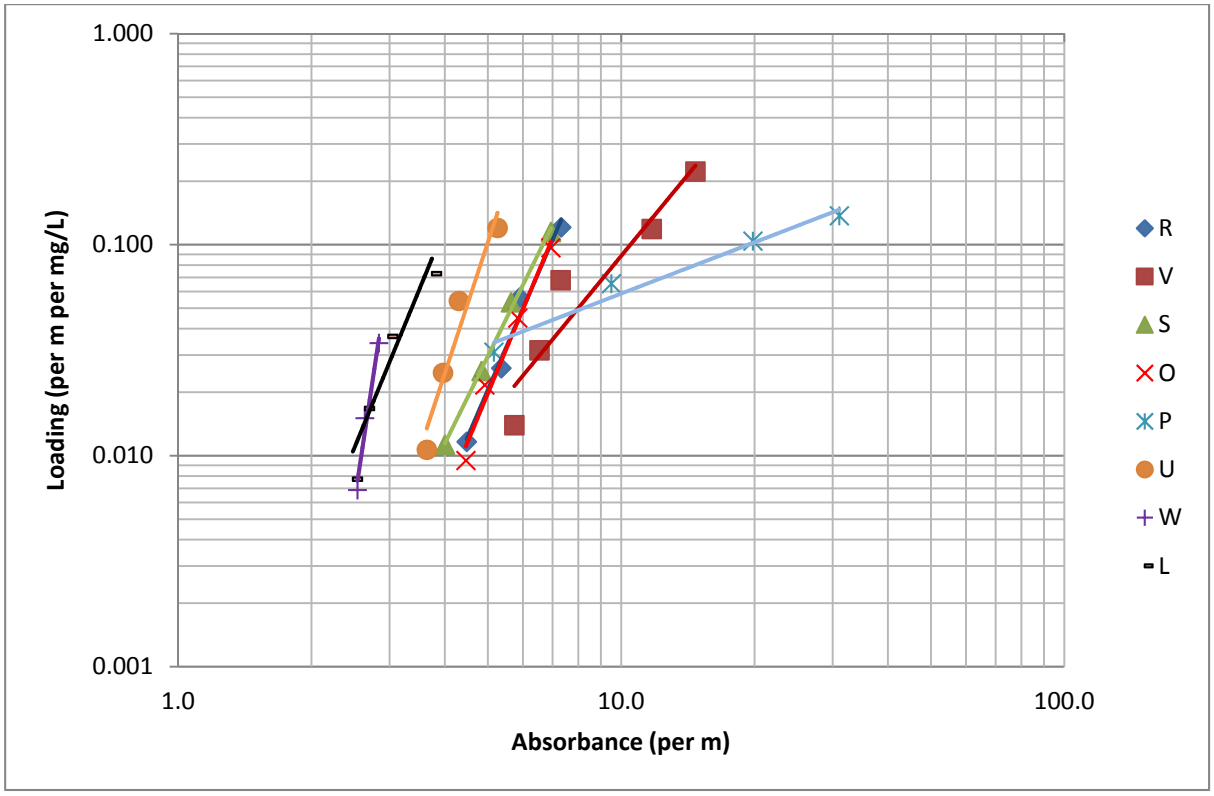

Figure 6.Freundlich isotherms with MP 600 for round 3 samples.

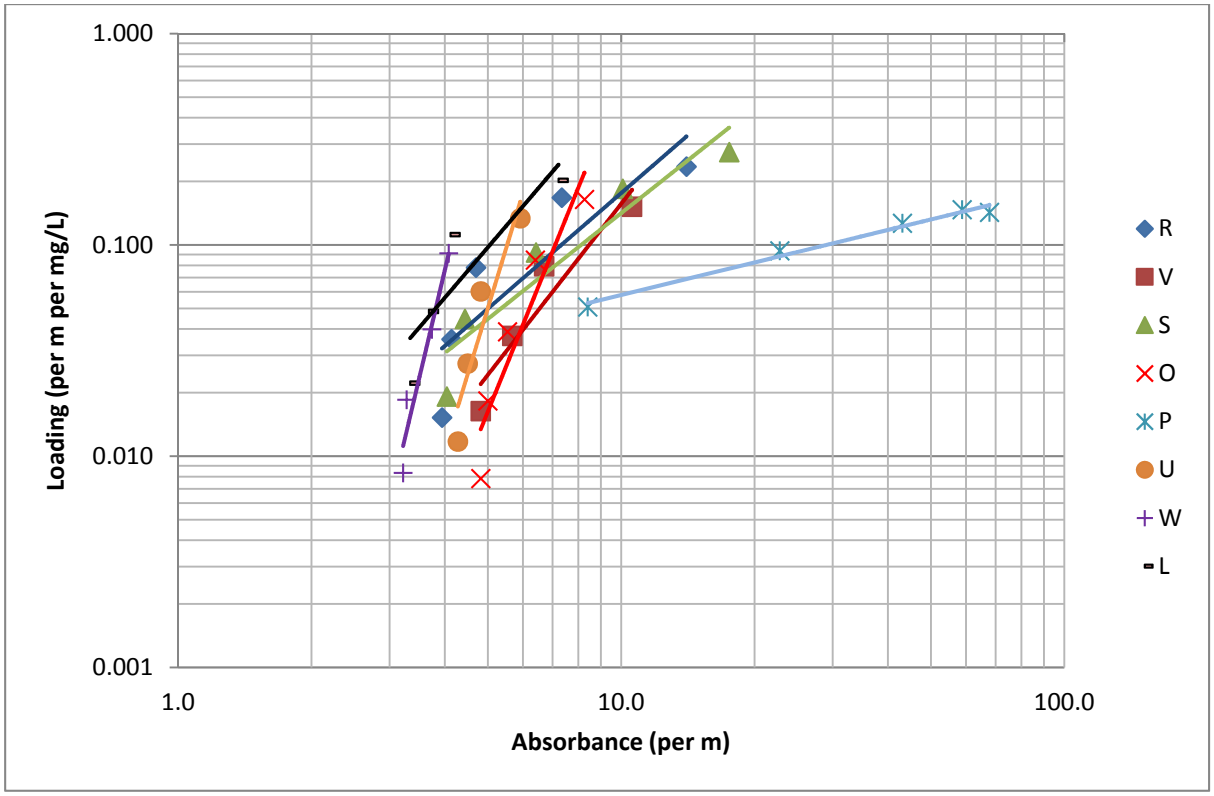

Figure 7. Freundlich isotherms with MP 600 for round 4 samples.

CONCLUSION

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